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Preparation and ^{13}C NMR study on 1-aryl-3,3-difluoro-2-(phenylethynyl)-cyclopropenes: long distance Hammett substituent effect

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ABSTRACT

Coupling of 1-aryl-3,3-difluoro-2-chlorocyclopropenes and phenylacetylene using Sonogashira reaction with $Pd(OAc)_2$ and CuI as the catalyst with K_2CO_3 as a base yields phenylethynylcyclopropenes in high selectivity and good yields. The ^{13}C chemical shifts of Cε of ~105 ppm on acetylene group significantly different from phenylacetylene (84 ppm) suggest that the acetylene group possesses less sp hybrid character due to an unusual long distance Hammett substituent effect. It is also confirmed by the substituent parameter analysis, while the Cβ and Cε display the strong resonance effect (their values are 6.89 and 3.37, respectively).

1. Introduction

The reaction of dihalocarbene (X=Cl, Br) and an olefin is an important process for preparing dihalocyclopropanes[1] while much less is known about the addition of difluorocarbene to the styrene.[2] We have previously attempted to add dihalocarbene (X=Br, Cl), via the reaction of haloform and NaOH, to 2,2-difluorostyrenes for preparing difluorocyclopropanes. However, under the presence of a strong base, dihalocyclopropanes underwent an elimination of HX to form 1-aryl-3,3-dihalo-2-halocyclopropenes.[3] Among the coupling reactions,[4] Sonogashira coupling reactions were employed for coupling the aryl halides and arylacetylene catalyzed by Pd complex and Cu(I) in the presence of a suitable base.[5] In this work, we search the conditions for Sonogashira coupling reaction of chlorocyclopropenes and phenylacetylene to yield a series of 1-aryl-2-phenylethynylcyclopropenes for ^{13}C NMR study.

In our previous studies on the substituent effect on the chemical shifts (SCS) of carbon on cyclopropanes, we found that the chemical shifts of Cβ and Cγ strongly depend on the substituents on the phenyl ring,[6] namely, the substituents on the phenyl ring affect the chemical shifts of Cβ via the field effect and those of Cγ via the resonance effect. The finding is rationalized in terms of the ability of the three-membered ring to transmit the electron cloud. The substituent effect on the chemical shifts of carbon on the 1-aryl-3,3-difluoro-2-halocyclopropenes was also sensitive to the resonance effect on the carbon bearing halogen and the field effect on the carbon bearing fluorine atoms.[7] In this new series of compounds, which contains an additional triple bond on the Cβ conjunction to the cyclopropene ring, the extension of the substituent effect is expected to take place. Herein, we report the unusual long distance resonance effect on the 1-aryl-3,3-difluoro-2-phenylethynyl-cyclopropenes. The correlation between the SCS and the Hammett constants will be discussed.

2. Results and discussion

Although the coupling reaction between 3,3-difluoro-2-iodocyclopropenes with terminal alkynes had been reported,[8] in this work, less active cyclopropenes, i.e., chloro-counterpart was used as the precursors for preparing a series of *gem*-difluorocyclopropenylalkynes. In order to find the optimal reaction conditions for the reaction of **1a** and **2** to yield the cross-coupling products **3**, various factors—such as catalysts, solvents, and temperature—were investigated (Scheme 1). In most cases under study, the homo-coupling product, i.e., 1,4-diphenylbutadiynes **4**, was obtained from phenylacetylene in the presence of various catalysts, solvents, and bases (Table 1). However, cross-coupling products were mainly obtained in the presence of $Pd(OAc)_2$, CuI, HMPA, and K_2CO_3 in CH_3CN solution (entry 13). In general, the formation of homo-coupling product **4** is favored in reactions at higher

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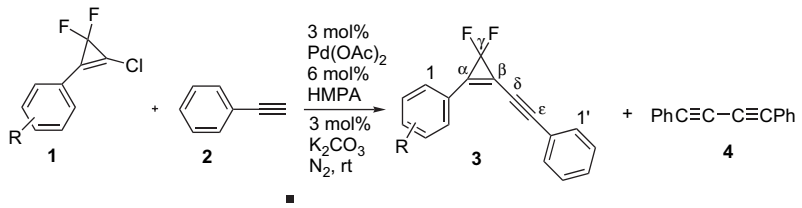

Scheme 1.

Table 1
Competition between cross- and homo-coupling reactions of 1-aryl-3,3-difluoro-2-chlorocyclopropene **1a** and phenylacetylene **2** under various conditions[a]

Entry	Solvent	Catalyst[b]	Base	Temperature (°C)	Yield (%)	
					Cross-coupling product	Homo-coupling product
1	THF	A	Et_3N	rt	40	45
2	THF	A	Et_3N	80	5	80
3	THF	B	Et_3N	rt	5	8
4	DMF	B	Et_3N	rt	5	15
5	DMF	C	Et_3N	rt	3	20
6	DMF	C	Et_3N	80	4	90
7	DMF	D	Et_3N	rt	5	30
8	C_6H_6	D	Et_3N	80	3	88
9	DMF	E	Et_3N	80	3	90
10	Et_3N	B	Et_3N	rt	5	24
11	Et_3N	D	Et_3N	rt	4	12
12	CH_3CN	B	Et_3N	rt	5	15
13	CH_3CN	F	K_2CO_3	rt	92(65)[c]	6
14	CH_3CN	F	K_2CO_3	rt	0[d]	90

[a] Reaction time: 2 h; the yields were based on the GC analysis.
[b] The catalysts are Pd (3 mol %) and Cu (6 mol %) complexes. Their combination are as following: A: $PdCl_2(PPh_3)_2$, CuI, PPh_3; B: $PdCl_2(PPh_3)_2$, CuI; C: $PdCl_2(PPh_3)_2$, CuCl; D: $Pd(PPh_3)_4$, CuI; E: $Pd(PPh_3)_4$, CuCl; F: $Pd(OAc)_2$, CuI, HMPA (6 mol %).
[c] Isolated yield.
[d] Reaction of 1-chloro-2-phenylcyclopropene and phenylacetylene.

temperatures. A treatment of unfluorinated analogues and phenylacetylene under the same conditions also yields the homo-coupling product **4** (entry 14). Unusual character of difluorochlorocyclopropene **1** might be due to that it processes an aromaticity based on the calculated and observed bond length and dipole moment of *gem*-difluorocyclopropene in which consists with the delocalization of electron density via a negative hyperconjugation from π-bond into the C–F σ* orbitals.[9] With the reaction conditions of entry 13, a series of 3,3-difluorocyclopropenyl-alkynes were synthesized (Scheme 1).

In general, the chemical shifts of the carbon of the difluorocyclopropene series resonate at the down-field region due to the effect of sp^2 orbital and the presence of two fluorine atoms (Table 2). In the proton-decoupled ^{13}C NMR spectra, carbons displaying triplet patterns areresulted from their coupling with two fluorine atoms on the Cγ. The ^{13}C NMR chemical shifts for the Cε (acetylenic carbon) move down-field substantially, 105.3 ppm for **3a** compared with 84.0 ppm for **2** for the same carbon (Table 2). This down-field shift is also observed for its unfluorinated counterpart, 1-phenyl-2-phenylethynylcyclopropene (**7**, 104 ppm).[10] The combination of up-field shift for Cβ and down-field shift for Cε strongly indicates the operation of resonance effect between the cyclopropene ring and triple bond with a possible extend to another phenyl ring through a triple bond, which causes a loss of sp character of acetylene and lowers the ring strain energy on the cyclopropene ring.

Table 2
Comparison of the ^{13}C chemical shifts of carbons on cyclopropene ring and the triple bond

Compound	α (ppm)	β (ppm)	γ (ppm)	δ (ppm)	ε (ppm)
3a	130.1	108.8	100.9	73.3	105.3
7	132.8	108.3	25.6	79.7	104.3
1a	128.2	113.7	100.7		
2	—	—	—	77.9	84.0

The Hammett constants (σ) are values reflecting the total resonance and field effect on the substituent effect on the chemical shifts of the second substituent.[11] Inspecting the ^{13}C chemical shifts for the compounds containing various substituents, we found that the chemical shifts of Cα, Cβ, Cγ, Cδ, and Cε depend on the substituents (Table 3). The SCS values for this series of compounds along with Hammett constants (σ) are summarized in Table 3. While Cα and Cδ change irregularly, Cβ and Cε shift up-field when the substituents on the aromatic rings are electron-donor group, and vice versa; and Cγ behaves in the other way. Both phenomena correlate well with Hammett substituent constants (σ).

The plot for the SCS values versus σ values is shown in Figure 1. There appear to be the inflections in the correction lines, which correspond to the slope of +6.89 (R^2=0.894), +3.37 (R^2=0.959), and −0.97 (R^2=0.926) for the groups varying from *p*-methoxy to *m*-bromo for Cβ, Cε, and Cγ, respectively. The positive slopes suggest that SCS effect by the substituent on the aryl ring is attributed directly to the resonance effect. On the other hand, the negative values for Cγ indicate the field effect. However, the long range

Table 3
The SCS value of the carbons of cyclopropene (Cα, Cβ, Cγ) and acetylene (Cδ, Cε) groups for various substituents on the benzene ring[a]

R	σ	Cα	Cβ	Cγ	Cδ	Cε
4-OCH_3	−0.27	−0.40	−3.62	0.17	0.33	−1.37
4-CH_3	−0.17	−0.04	−1.4	0.09	0.20	−0.54
3-CH_3	−0.07	0.07	−0.37	0.05	0.03	−0.18
H	0	(130.06)	(108.79)	(100.94)	(73.30)	(105.34)
3-OCH_3	0.12	−0.01	0.30	−0.01	−0.01	0.16
4-Cl	0.23	−1.24	0.70	−0.32	−0.14	0.61
4-Br	0.23	−1.08	0.94	−0.31	−0.07	0.74
3-Cl	0.38	−1.49	1.86	−0.42	−0.26	1.09
3-Br	0.39	−1.64	1.88	−0.44	0.34	1.11
Slope			+6.89	−0.97		+3.37
R^2			0.894	0.926		0.959

[a] The SCS values represent the differences between chemical shifts of the compound under study and the unsubstituted compound **1a**. The positive value indicates more down-field shift.

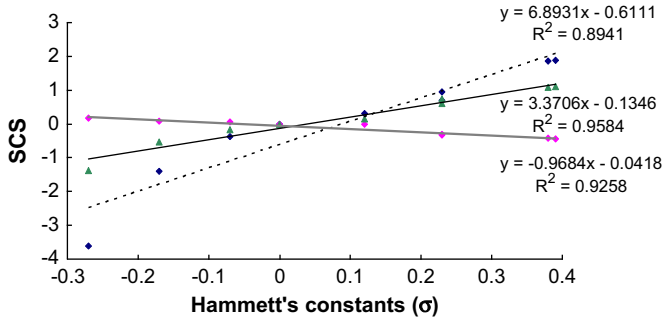

Figure 1. The correction between SCS (C_β (◆), C_γ (◆), C_ε (▲)) versus Hammett's constants (σ).

resonance effect on Cε by the aryl group (slope=+3.37) through four bonds is characteristic for this system. The contribution of resonance between the triple bond and double bond enhances the resonance effect for the cyclopropene ring leading to a larger ρ value of 6.89 as compared to the value of 4.50 found for compound **1** series. On the other hand, the substituent effect on Cγ is reduced (ρ=−0.97 compared with −1.63 for compound **1**).[9]

3. Conclusion

The difluorocyclopropene compounds have a unique character, i.e., activated the carbon–chlorine bond for the Sonogashira reaction and transmitted the electron from a phenyl ring through the acetylene moiety. This behavior is attributed to the aromaticity of cyclopropene resulting from the low-lying antibonding σ* orbitals of the C–F σ-bonds, which are capable of accepting π-electrons from an adjacent carbon.

4. Experimental

4.1. General

2,2-Difluorostyrenes were prepared from the corresponding aldehydes and $ClCF_2CO_2Na$ in the presence of triphenylphosphine in dry diglyme solution at 180 °C.[12] 1-Aryl-2-chloro-3,3-difluorocyclopropenes were prepared from the reaction of 2,2-difluorostyrene and chloroform in the presence of NaOH.[9] The preparation of phenylethynylcyclopropenes was performed under a dry nitrogen atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 400, 100, and 376 MHz on Bruker Advance 400 spectrometer, respectively, at ambient temperature. Chemical shifts for samples in $CDCl_3$ solution are reported in δ units relative to TMS (^{1}H and ^{13}C) and trifluoromethylbenzene (at −63.9 ppm, ^{19}F). For the SCS study, the ^{13}C NMR data of 0.03 g analyte in 0.3 mL of $CDCl_3$ solution were recorded at 100 MHz. The digital resolution was generally 0.02 ppm. Mass spectra were obtained from GC/MS (Fisons 8000 series coupled with Finnigan MD-800) at an ionization potential of 70 eV. IR spectra were recorded from a film on KBr plate on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed at the Instrumental Analytic Center at National Chung-Hsing University.

4.2. Preparation of 1-aryl-3,3-difluoro-2-phenylethynylcycloropenes via Sonogashira coupling reaction

Typical procedure: Under a nitrogen atmosphere, $Pd(OAc)_2$ (6.6 mg, 0.03 mmol) and K_2CO_3 (0.42 g, 3 mmol) were placed in a 10 mL side-armed Pyrex tube using a magnetic stirring bar. The system was evacuated when heated at 60 °C for 30 min to remove the moisture and oxygen molecule. After the system was refilled with nitrogen, CH_3CN (5 mL), HMPA (11 mg, 0.06 mmol), 1-phenyl-3,3-difluoro-2-chlorocyclopropene (186 mg, 1 mmol), and phenylacetylene (110 mg, 1.1 mmol) were added against a stream of nitrogen followed by addition of $Pd(OAc)_2$. After the mixture was stirred at room temperature for 2 h, it was filtered and solvent was removed under reduced pressure. Next, the residue was purified by flash chromatography on a silica gel column to give 163 mg the cross-coupling compound. Yield is given below.

*4.2.1. 1-Phenyl-3,3-difluoro-2-phenylethynylcyclopropene (**3a**)*

Yield 65%; yellow solid; mp 36–37 °C; ^{1}H NMR δ 7.79 (dd, 2H, J=8, 2 Hz, $C_{2,6}$-H), 7.69 (dd, 2H, J=8, 2 Hz, $C_{2',6'}$-H), 7.58–7.64 (m, 3H, $C_{3,4,5}$-H), 7.40–7.51 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 73.3, 100.9 (t, J=279 Hz), 105.3, 108.8 (t, J=12 Hz), 121.7, 129.7, 130.1 (t, J=10 Hz), 130.4, 130.9, 131.4, 133.1, 133.2; ^{19}F NMR δ −107.6; IR 2204, 1768 ($\nu_{C=C}$) cm^{-1}; MS m/z (%) 252 ($M^{+\bullet}$, 80.5), 251 (100.0), 233 (20.9), 202 (69.2), 200 (32.2); calcd for $C_{17}H_{10}F_2$: C, 80.94; H, 4.00; found: C, 81.02; H, 4.06.

*4.2.2. 1-(3′-Tolyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3b**)*

Yield 66%; yellow solid; mp 38–39 °C; ^{1}H NMR δ 7.68 (dd, 2H, J=8, 2 Hz, $C_{2',6'}$-H), 7.59 (br, 1H, C_2-H), 7.45–7.54 (m, 6H, $C_{3,4,5}$, $C_{3',4',5'}$-H), 2.42 (s, 3H, CH_3); ^{13}C NMR δ 21.0, 73.3, 101.0 (t, J=279 Hz), 105.2, 108.4 (t, J=12 Hz), 121.6, 124.0, 129.7, 130.1 (t, J=10 Hz), 130.3, 131.2, 131.4, 133, 134.0, 140.4; ^{19}F NMR δ −108.3; IR 2204, 1768 ($\nu_{C=C}$) cm^{-1}; MS m/z (%) 266 ($M^{+\bullet}$,100), 265 (46), 251 (96), 216 (63), 215 (72), 189 (20); calcd for $C_{18}H_{12}F_2$: C, 81.19; H, 4.52; found: C, 81.17; H, 4.40.

*4.2.3. 1-(4′-Tolyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3c**)*

Yield 71%; yellow solid; mp 40–42 °C; ^{1}H NMR δ 7.70 (d, 2H, J=8 Hz, $C_{2,6}$-H), 7.67 (dd, 2H, J=8, 2 Hz, $C_{2'6'}$-H), 7.42 (d, 2H, J=8 Hz, $C_{3,5}$-H), 7.45–7.54 (m, 6H, $C_{3,4,5}$-H, $C_{3',4',5'}$-H), 2.43 (s, 3H, –CH_3); ^{13}C NMR δ 21.7, 73.5, 101.0 (t, J=279 Hz), 104.8, 107.4 (t, J=12 Hz), 121.4, 121.8, 129.7, 130.0 (t, J=10 Hz), 131.0, 131.1, 131.3, 133.0, 144.2; ^{19}F NMR δ −107.8; IR 2203, 1766 ($\nu_{C=C}$) cm^{-1}; MS m/z (%) 266 ($M^{+\bullet}$, 92), 265 (42), 251 (100), 216 (71), 215 (87); calcd for $C_{18}H_{12}F_2$: C, 81.19; H, 4.52; found: C, 81.14; H, 4.47.

*4.2.4. 1-(3′-Anisyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3d**)*

Yield 69%; yellow solid; mp 38–40 °C; ^{1}H NMR δ 7.69 (dd, 2H, J=8, 2 Hz, $C_{2'6'}$-H), 748–7.55 (m, 4H, C_5-H, $C_{3',4',5'}$-H), 7.37 (d, 1H, J=8 Hz, C_6-H), 7.20 (dd, 1H, J=8, 2 Hz, C_4-H), 3.90 (s, 3H, OCH_3); ^{13}C NMR δ 55.9, 73.3, 100.9 (t, J=279 Hz), 105.5, 109.1 (t, J=12 Hz), 115.4, 119.4, 121.7, 123.3, 125.2, 129.8, 130.0 (t, J=10 Hz), 131.5, 131.6, 133.1, 161.2; ^{19}F NMR δ −107.5; IR 2204, 1768 ($\nu_{C=C}$) cm^{-1}; MS m/z (%) 282 ($M^{+\bullet}$,100), 267 (62), 251 (45), 238 (71), 232 (42), 202 (25), 189 (35); calcd for $C_{18}H_{12}F_2O$: C, 76.59; H, 4.28; found: C, 76.48; H, 4.28.

*4.2.5. 1-(4′-Anisyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3e**)*

Yield 70%; yellow solid; mp 71–73 °C; ^{1}H NMR δ 7.74 (d, 2H, J=8 Hz, C_2-H), 7.68 (dd, 2H, J=8, 2 Hz, $C_{2',6'}$-H), 7.48–7.52 (m, 3H, $C_{3',4',5'}$-H), 7.16 (d, 2H, J=8 Hz, $C_{3,5}$-H), 3.91 (s, 3H, OCH_3); ^{13}C NMR δ 56.1, 73.6, 101.1 (t, J=279 Hz), 105.9, 106.2 (t, J=12 Hz), 115.9, 116.7, 121.9, 129.7 (t, J=10 Hz), 129.7, 131.2, 132.9, 133.0, 163.9; ^{19}F NMR δ −107.6; IR 2205, 1766 ($\nu_{C=C}$) cm^{-1}; MS m/z (%) 282 ($M^{+\bullet}$, 100), 267 (40), 251 (24), 238 (63), 217 (49), 189 (57); calcd for $C_{18}H_{12}F_2O$: C, 76.59; H, 4.28; found: C, 76.57, H, 4.25.

*4.2.6. 1-(3′-Chlorophenyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3f**)*

Yield 63%; yellow solid; mp 49–51 °C; ^{1}H NMR δ 7.81 (br, 1H, C_2-H), 7.70–7.81 (m, 1H, C_6-H), 7.68 (dd, 2H, J=8, 2 Hz, $C_{2',6'}$-H), 7.58–7.65 (m, 2H, $C_{4,5}$-H), 7.47–7.55 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 73.0, 100.5 (t, J=280 Hz), 106.4, 110.7 (t, J=12 Hz), 121.4, 125.8, 128.6 (t, J=10 Hz), 129.4, 129.8, 130.2, 131.6, 132.2, 133.0, 133.2,

135.7; ^{19}F NMR δ −107.6; IR 2205, 1769 ($\nu_{C=C}$) cm^{-1}; MS *m*/*z* (%) 288 (15), 286 ($M^{+\bullet}$, 43), 251 (100), 238 (14), 236 (39), 200 (35); calcd for $C_{17}H_9ClF_2$: C, 71.22; H, 3.16; found: C, 71.27; H, 3.13.

*4.2.7. 1-(4′-Chlorophenyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3g**)*

Yield 60%; yellow solid; mp 71–73 °C; ^{1}H NMR δ 7.82 (d, 2H, *J*=8 Hz, $C_{3,5}$-H), 7.68 (dd, 2H, *J*=8, 2 Hz, $C_{2',6'}$-H),7.65 (d, 2H, *J*=8 Hz, $C_{2,6}$-H), 7.48–7.58 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 73.2, 100.6 (t, *J*=280 Hz), 105.9, 109.5 (t, *J*=12 Hz), 121.5, 122.8, 128.8 (t, *J*=10 Hz), 129.8, 130.7, 131.5, 132.5, 133.1, 138.7; ^{19}F NMR δ −107.7; IR 2203, 1769 ($\nu_{C=C}$) cm^{-1}; MS *m*/*z* (%) 288 (13), 286 ($M^{+\bullet}$, 36), 251 (100), 238 (15), 236 (43), 200 (37); calcd for $C_{17}H_9ClN_2$: C, 71.22; H, 3.16; found: C, 71.24; H, 3.22.

*4.2.8. 1-(3′-Bromophenyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3h**)*

Yield 67%; yellow solid; mp 52–53 °C; ^{1}H NMR δ 7.95 (t, 1H, *J*=8 Hz, C_2-H), 7.76–7.88 (m, 2H, $C_{2,6}$-H), 7.69 (dd, 2H, *J*=8, 2 Hz, $C_{2',6'}$-H), 7.59 (t, 1H, *J*=8 Hz, C_5-H), 7.48–7.58 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 73.0, 100.5 (t, *J*=280 Hz), 106.4, 110.6 (t, *J*=12 Hz), 121.4, 123.6, 126.0, 128.4 (t, *J*=10 Hz), 129.8, 131.6, 132.4, 133.2, 136.0; ^{19}F NMR δ −107.5; IR 2205, 1769 ($\nu_{C=C}$) cm^{-1}; MS *m*/*z* (%) 332 (23), 330 ($M^{+\bullet}$,25), 282 (15), 280 (16), 251 (100), 200 (43); calcd for $C_{17}H_9BrF_2$: C, 61.66; H, 4.54; found: C, 61.60, H, 4.58.

*4.2.9. 1-(4′-Bromophenyl)-3,3-difluoro-2-phenylethynylcyclopropene (**3i**)*

Yield 62%; yellow solid; mp 75–76 °C; ^{1}H NMR δ 7.82 (d, 2H, *J*=8 Hz, $C_{3,5}$-H), 7.74 (d, 2H, *J*=8 Hz, $C_{2,6}$-H), 7.69 (dd, 2H, *J*=8, 2 Hz, $C_{2',6'}$-H), 7.48–7.58 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 73.2, 100.6 (t, *J*=280 Hz), 106.1, 109.7 (t, *J*=12 Hz), 121.6, 123.2, 127.2, 129.0 (t, *J*=10 Hz), 129.8, 131.6, 132.6, 133.1, 133.7; ^{19}F NMR δ −108.4; IR 2204, 1771 ($\nu_{C=C}$) cm^{-1}; MS *m*/*z* (%) 332 (22), 330 ($M^{+\bullet}$,23), 282 (18), 280 (19), 251 (100), 200 (40); calcd for $C_{17}H_9BrF_2$: C, 61.66; H, 2.74; found: C, 61.61; H, 2.78.

*4.2.10. 3,3-Difluoro-1-naphthyl-2-phenylethynylcyclopropene (**6**)*

Yield 19%; yellow solid; mp 83–85 °C; ^{1}H NMR δ 8.46 (d, 1H, *J*=8 Hz, C_8-H), 8.19 (d, 1H, *J*=8 Hz, C_5-H), 8.06 (d, 1H, *J*=8 Hz, C_4-H), 8.01 (d, 1H, *J*=8 Hz, C_2-H), 7.82 (t, 1H, *J*=8 Hz, C_3-H), 7.75 (d, 2H, *J*=8 Hz, $C_{6,7}$-H), 7.69 (dd, 2H, *J*=8, 2 Hz, $C_{2',6'}$-H), 7.48–7.58 (m, 3H, $C_{3',4',5'}$-H); ^{13}C NMR δ 74.1, 100.5 (t, *J*=279 Hz), 105.9, 108.7 (t, *J*=12 Hz), 121.2, 121.6, 124.9, 126.6, 128.0, 128.3 (t, *J*=10 Hz), 129.3, 129.8, 129.9, 131.5, 132.0, 132.3, 133.1, 134.3, 134.6; ^{19}F NMR δ −107.5; IR 2202, 1764 ($\nu_{C=C}$) cm^{-1}; MS *m*/*z* (%) 302 ($M^{+\bullet}$,71), 301 (100), 283 (26), 250 (28), 225 (30); calcd for $C_{21}H_{12}F_2$: C, 83.43; H, 4.00; found: C, 83.45; H, 3.92.

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References and notes

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